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(REV 5-93)

US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY DOCKET NUMBER  
2001-0574ATRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371U.S. APPLICATION NO.  
(if known, enter 35 U.S.C. §371)  
[NEW] 097831451International Application No.  
PCT/EP98/07174International Filing Date  
November 10, 1998

Priority Date Claimed

**Title of Invention**

PROCESS FOR PRODUCING CALCIUM COMPOUNDS CONTAINING WATER OF CRYSTALLIZATION

**Applicant(s) For DO/EO/US**


Josef LEHMKUHL; Ansgar FENDEL; Hubert BINGS

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371,
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. §371(c)(2)). **ATTACHMENT A**
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)).
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19.
9. ☒ An **unexecuted** oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). **ATTACHMENT B**
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

**Items 11. to 14. below concern other document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98. **ATTACHMENT C**
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment. **ATTACHMENT D**
  - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☒ Other items or information:
  - a. Cover Page of Published International Application WO 00/27752 - **ATTACHMENT E**
  - b. International Search Report - **ATTACHMENT F**

U.S. APPLICATION NO. <b>09/831451</b> [NEW]		INTERNATIONAL APPLICATION NO. PCT/EP98/07174		ATTORNEY'S DOCKET NO. 2001-0574A					
15. [X] The following fees are submitted  <b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee nor international search fee paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1000.00 International Search Report has been prepared by the EPO or JPO ..... \$ 860.00 International preliminary examination fee not paid to USPTO but international search paid to USPTO ..... \$ 710.00 International preliminary examination fee paid to USPTO but claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$ 690.00 International preliminary examination fee paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$ 100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <th style="width:50%;">CALCULATIONS</th> <th style="width:50%;">PTO USE ONLY</th> </tr> <tr> <td style="height: 100px; vertical-align: bottom;">\$860.00</td> <td></td> </tr> </table>		CALCULATIONS	PTO USE ONLY	\$860.00	
CALCULATIONS	PTO USE ONLY								
\$860.00									
Surcharge of \$130.00 for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).									
Claims	Number Filed	Number Extra	Rate						
Total Claims	17 -20 =	0	X \$18.00						
Independent Claims	1 - 3 =	0	X \$80.00						
Multiple dependent claim(s) (if applicable)			+ \$270.00						
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$860.00					
[X] Small Entity Status is hereby asserted. Above fees are reduced by 1/2.				\$430.00					
<b>SUBTOTAL =</b>				\$430.00					
Processing fee of \$130.00 for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+					
<b>TOTAL NATIONAL FEE =</b>				\$430.00					
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40 per property				+					
<b>TOTAL FEES ENCLOSED =</b>				\$430.00					
				Amount to be refunded	\$				
				Amount to be charged	\$				
a. [X] A check in the amount of \$ <u>430.00</u> to cover the above fees is enclosed. A duplicate copy of this form is enclosed. b. [ ] Please charge my Deposit Account No. 23-0975 in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. [ ] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-0975</u> .									
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or          (b)) must be filed and granted to restore the application to pending status.</b>									
19. CORRESPONDENCE ADDRESS   <div style="text-align: center;">   <b>000513</b>          PATENT TRADEMARK OFFICE       </div>			By: <u>Matthew Jacob</u> Matthew Jacob, Registration No. 25,154  WENDEROTH, LIND & PONACK, L.L.P. 2033 "K" Street, N.W., Suite 800 Washington, D.C. 20006-1021 Phone: (202) 721-8200 Fax: (202) 721-8250  May 10, 2001						

[CHECK NO. 44417]

[2001-0574A]

09/831451

JC08 Rec'd PCT/PTO 10 MAY 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :  
Josef LEHMKUHL et al. : Attn: BOX PCT  
Serial No. [NEW] : Docket No. 2001-0574A  
Filed May 10, 2001 :  
PROCESS FOR PRODUCING CALCIUM :  
COMPOUNDS CONTAINING WATER OF :  
CRYSTALLIZATION :  
[Corresponding to PCT/EP98/07174  
Filed November 10, 1998]

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents,  
Washington, DC 20231

Sir:

In the interest of compact prosecution and to reduce PTO filing fees, please amend the present application as follows:

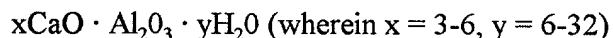
IN THE CLAIMS:

Please cancel Claims 1 to 17 without prejudice to the subject matter thereof and add the following claims in their place:

18. (New) A process for producing calcium compounds containing water of crystallization, wherein

a) by a chemical reaction between an aqueous alkaline solution of sodium aluminate and a solid or dissolved and suspended, respectively, calcium (hydr)oxide in the presence of carbon dioxide a precipitate of a mixture of calcium aluminatohydrates having the following modular formula is formed:

ATTACHMENT D



- b) the thus obtained precipitate, in a manner known per se, is separated by sedimentation, dehydrated, washed with water and the thus obtained filter cake is optionally dried;
- c) the filter cake obtained in step (b) in a wet and/or dried form is suspended in water and added with at least one mineral acid and/or at least one salt thereof for forming a calcium aluminatesalt precipitate containing water of crystallization,
- d) the precipitate, in a manner known per se, is separated by sedimentation, dehydrated, washed with water and the thus obtained filter cake is crushed and optionally dried and/or milled.

19. **(New)** The process according to claim 18, wherein an aqueous alkaline sodium aluminate solution a waste pickling lye is used as obtained by surface-treatment of aluminum metal.

20. **(New)** The process according to claim 18, wherein an aqueous alkaline sodium aluminate solution and a waste pickling lye, respectively, is used wherein  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  are present in a mole ratio of (1.0 to 10.0):1, preferably of (1.2 to 2.5):1.

21. **(New)** The process according to claim 18, wherein in step (a) an aqueous alkaline sodium aluminate solution is used as a starting material and calcium (hydr)oxide is added thereto.

22. **(New)** The process according to claim 18, wherein in step (a) calcium (hydr)oxide is used as a starting material and then the aqueous alkaline sodium aluminate solution is added.

23. **(New)** The process according to claim 21, wherein from 2 to 8 mole of  $\text{CaO}$  equivalents, preferably from 3 to 5 mole of  $\text{CaO}$  equivalents, based on 1 mole of  $\text{Al}_2\text{O}_3$  equivalent, are added.

24. (New) The process according to claim 18 wherein the precipitation of the precipitate in step (a) is carried out within a reaction time of from 5 to 3000 min, preferably from 60 to 600 min, at a temperature of from 5 to 60°C, preferably from 30 to 50°C.

25. (New) The process according to claim 18, wherein in that the calcium aluminatehydrate precipitate in step (b) is mechanically dehydrated, preferably by using a pressure filtration, in particular by using a chamber filter press or a membrane filter press and, alternatively, by using a vacuum belt filter or a centrifuge.

26. (New) The process according to claim 25, wherein the dehydrated calcium aluminatehydrate precipitate at a temperature of  $< 100^{\circ}\text{C}$  is dried and crushed, preferably milled.

27. (New) The process according to claim 25, wherein the dehydrated calcium aluminatehydrate precipitate at a temperature of from 100 to  $1300^{\circ}\text{C}$ , preferably from 100 to  $500^{\circ}\text{C}$ , is dried and calcined, respectively, and crushed, preferably milled.

28. (New) The process according to claim 18, wherein the dehydrated and optionally washed filter cake of step (b) is suspended in water and added with at least one mineral acid and/or at least one salt thereof to form an extra white calcium aluminatesalt precipitate containing water of crystallization, the precipitate optionally being further processed, wherein the dehydrated calcium aluminatehydrate precipitate at a temperature of  $< 100^{\circ}\text{C}$  is dried and crushed, preferably milled.

29. (New) The process according to claim 28, wherein as a mineral acid hydrochloric acid, hydrofluoric acid, sulfuric acid, silicic acid and/or carbonic acid and salts thereof, respectively, in particular their alkaline metal salts, alkaline earth metal salts and aluminum salts are used.

30. (New) The process according to claim 29, wherein as a mineral acid a sulfuric acid containing aluminum, preferably a waste acid derived from eloxal plants, is used.

31. (New) The process according to claim 28, wherein in step (b) a sulfate is added to the filter cake suspended in water in a ratio of 1 part by weight of Al to 4 to 7 parts by weight of  $\text{SO}_4$ , based on the total aluminum content.

32. (New) The process according to claim 31, wherein anions of the further mineral acid(s) which are hydrochloric acid, hydrofluoric acid, sulfuric acid, silicic acid and/or carbonic acid and salts thereof, respectively, in particular their alkaline metal salts, alkaline earth metal salts and aluminum salts are used and are additionally added in amounts of 1 part by weight of Al to 0.5 to 10 parts by weight of anions, based on the total aluminum content of the suspension.

33. (New) A method for use of the products obtained in the process according to claim 18 in the form of an aqueous suspension and/or in solid form as an extra white pigment for surface-coating of paper or as a filler in the production of paper or in the production of paints and lacquers, preferably for indoor and outdoor uses.

34. (New) A method for use of the products obtained in the process according to claim 18 as a flame-retardant filler for fire-protecting construction materials, insulating materials, mortars, wallpapers, paperboards, papers, for the production of paints and lacquers, as a filler for producing plasterboards or building slabs or as an hydraulically active additive for producing swelling cements, swelling plasters and screeds, for microfiber armation of cements and mortars or as a swelling component for the production of explosion-protected explosives.

**REMARKS**


The above amendment is presented to eliminate multiple dependency, including improper multiple dependent claims, thereby reducing PTO filing fees.

Moreover, use claims have been converted to method claims.

Favorable action on the merits is now requested.

Respectfully submitted,

Josef LEHMKUHL et al.

By   
Matthew Jacob  
Registration No. 25,154  
Attorney for Applicants

MJ/pjm  
Washington, D.C. 20006-1021  
Telephone (202) 721-8200  
Facsimile (202) 721-8250  
May 10, 2001

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**Process for producing calcium compounds containing  
water of crystallisation**

- 15 The invention relates to the production and use of calcium compounds containing water of crystallisation, in particular of ionogenic bound compounds on calcium aluminatehydrate and calcium aluminatehydrate salt basis, preferably of the corresponding sulfates, silicates, carbonates, fluorides and/or chlorides. The thus obtained different compounds are useful as fillers or extra white pigments in the production and surface-coating of paper, paperboard or card, in the production of paints and lacquers, such as in the production of paints and lacquers for indoor and outdoor uses or for the rust-protection of metals, as a flame-retardant filler for fire-protecting construction materials, insulating materials, mortars, wallpapers, cardboards, papers and paints as well as fillers for
- 20 producing plasterboards and construction slabs, respectively, mortars, paints or as an hydraulically active additive for producing swelling cements, swelling plasters and screeds as well as a swelling component for explosion-protected explosives.
- 25
- 30 Fillers and additives, in particular mineral fillers and additives are used in great extent i.a. in the plastic, paint, tire and ceramic industries as well as in the construction material industries, in particular in pulp and paper industries.



Papier, paperboard and card are produced for example from an aqueous suspension essentially by dehydrating, drying and pressing it. Besides fiber materials like cellulose and wood chips, i.a. also fillers, preferably the natural minerals kaolin (aluminosilicates) and chalk (calcium carbonate) are used. Depending on the requirements in regard to the quality of paper and paperboard, respectively, (printability, whiteness, gloss, strength etc.) the amount of added fillers, however, is limited. Typically it is from 10 to 25 % by weight, based on the weight of the paper. In Germany in the paper industries about 3 millions of tons of fillers per year are consumed.

Mineral natural fillers have to be degraded, purified (for example washed) and milled. Higher quality demands of the filler processors have resulted in that more synthetic precipitates, preferably precipitated calcium carbonate, are used. Furthermore, several approaches have been made to use plaster (calcium sulfate) as a filler, in particular the reaction products obtained in vast amounts from fuming gas desulfurisation installations of power plants (REA plaster). However, until yet these were not successful since calcium sulfate is water-soluble up to a concentration of about  $2 \text{ g SO}_4^{2-}/\ell$  and no sufficient whiteness has been achieved. In the paper production an accumulation of dissolved calcium sulfate in the process water cycle occurs and therefore undesired deposits and microbiologic problems (for instance by bacteria like desulfovibrio or desulfazomaculum) arose.

In the paper industries a calcium aluminumsulfate precipitate is used as spreading pigment for high quality papers. This product is obtained from the starting materials aluminum sulfate and chalkhydrate according to the following reaction equation:



Since the above chemical reaction only proceeds spontaneously at a high pH of  $> 12$ , an excess of chalkhydrate is necessary. Furthermore, in this method

only suspensions having a solid content of  $< 50\%$  can be obtained, which are known i.a. as satin-white.

5 A further great application demand for mineral fillers exists in the construction industries. The development goes to prefabricated constructions and to the increased application of construction slabs. These should be as stabile as possible, heat-protecting and noise-protecting but nevertheless they should be lightweighted and having good fire-protecting properties. For this reason in an increasing extent construction slabs on plaster basis are produced either as  
10 plastercard slabs (outside card, inside plaster) or as plasterfiber slabs (for example mixtures of paper fibers and plaster). Plaster has a crystal water proportion of 2 mole and 21 % by weight, respectively. Therefore, a certain fire-protection is ensured. However, this fire-protection could be substantially improved with calcium aluminatesalt precipitates having a higher content of water  
15 of crystallisation.

A further application field is the production of insulating boards on fiber basis or other insulating materials. They are prepared from pulp, waste paper, waste  
20 textiles, coco and other fiber materials by pressing and they have to be made sufficiently fire-protecting by proper additives. As fire-protecting agents useful are mineral materials having a high content of water of crystallisation.

A further possibility for application of calcium aluminate products in the construction industries is their use as swelling components. In this case calcium  
25 aluminates and calcium sulfoaluminates are used the preparation thereof being carried out by sintering raw materials like bauxite, plaster and chalk at very high temperatures of up to  $1400^{\circ}\text{C}$ . This production is very cost and work intensive. An alternative low-cost preparation of swelling components would be highly  
30 desired.

Therefore, the object of the invention was to find crystal water-containing calcium compounds which can be easily produced as precipitates in a large scale

process and which can be used advantageously in the above-mentioned application fields.

It has been found that this object according to the present invention can be achieved by a process for producing calcium compounds containing water of crystallisation, the process being characterized in that

- a) by a chemical reaction between an aqueous alkaline solution of sodium aluminate and a solid or dissolved and suspended, respectively, calcium (hydr)oxide in the presence of carbon dioxide or carbonate a precipitate of a mixture of calcium aluminates having the following modular formula is formed:
 
$$x\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot z\text{CaCO}_3 \cdot y\text{H}_2\text{O} \text{ (wherein } x = 3-6, y = 6-32, z = 0-1) \text{ and}$$
- b) the thus obtained precipitate, in a manner known per se, is separated by sedimentation, dehydrated, optionally washed with water and the thus obtained filter cake is either dried and/or calcined and/or milled,
- c) or the filter cake obtained in step (b) in a wet and/or dried form is suspended in water and added with at least one mineral acid and/or at least one salt thereof for forming a calcium aluminatesalt precipitate containing water of crystallisation, the precipitate is separated by sedimentation, dehydrated, optionally washed with water and the thus obtained filter cake is crushed and optionally dried and/or milled.

As an aqueous alkaline sodium aluminate solution preferably a waste pickling lye as obtained in the surface-treatment of aluminum metal with caustic sodium is used.

A particularly preferably used aqueous alkaline sodium aluminate solution and waste pickling lye, respectively, is such one wherein  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  are present in a mole ratio of (1.0 to 10.0):1, preferably of (1.2 to 2.5):1.

- 5 According to a preferred embodiment of the invention in step (a) a diluted caustic sodium is used as the starting material and an alkaline sodium aluminate solution is then added and calcium hydroxide or calcium oxide in solid form or dissolved or suspended in caustic sodium is further added. The order of the addition of the sodium aluminate solution and of the calcium (hydr)oxide can  
10 also be reversed.

As calcium compound(s) preferably chalk milk (chalk hydrate or  $\text{Ca}(\text{OH})_2$ ) or burnt chalk ( $\text{CaO}$ ) is used.

- 15 The calcium compound(s) is (are) preferably used in an amount of from 2 to 8 mole of  $\text{CaO}$  equivalents, in particular from 3 to 5 mole of  $\text{CaO}$ -equivalents, based on 1 mole of  $\text{Al}_2\text{O}_3$  equivalent.

- The precipitation of the precipitate in step (a) is preferably carried out within a  
20 reaction time of from 5 to 3000 min, in particular from 60 to 600 min, at a temperature of from 5 to  $60^\circ\text{C}$ , preferably from 30 to  $50^\circ\text{C}$ . In doing this, a white precipitate of calcium aluminatehydrate containing crystal water is obtained.

- According to a preferred embodiment of the invention in step (b) the calcium  
25 aluminatehydrate precipitate is mechanically dehydrated, preferably by using a chamber filter press, a membrane filter press, a vacuum belt filter or a centrifuge.

- Thereafter, the crystallisation water-containing calcium aluminatehydrate pre-  
30 cipitate dehydrated and optionally washed with water at a temperature between 50 and  $200^\circ\text{C}$  is dried and crushed, preferably milled or at a temperature of

from 200 to 1300°C, preferably from 200 to 500°C, it is dried and calcined, respectively, and crushed, preferably milled.

- According to a further preferred embodiment of the invention in step (b) the filter cake dehydrated and optionally washed with water is suspended in water and in step (c) it is added with at least one mineral acid and/or at least one salt thereof to form a crystalline calcium aluminatesalt precipitate having a high content of crystallisation water.
- 10 To the filter cake suspended in water in step (b) in step (c) as a mineral acid preferably hydrochloric acid, hydrofluoric acid, sulfuric acid, silicic acid and/or carbonic acid and salts thereof, respectively, in particular their alkaline metal, alkaline earth metal and aluminum salts are added.
  - 15 To the filter cake obtained in step (b) and suspended in water, preferably a sulfate in the form of mineral acids or salts thereof is added in a ratio of 1 part by weight of Al to 4 to 7 parts by weight of SO<sub>4</sub>, based on the total aluminium content in the suspension.
  - 20 According to a further preferred embodiment of the invention anions of the above mentioned mineral acid(s) or/and salts thereof are additionally added in a ratio of 1 part by weight of aluminum to 0.5 to 10 parts by weight of anions, based on the total aluminum content of the suspension.
  - 25 The crystal water-containing precipitate obtainable in step (c) of the process of the present invention can be separated by sedimentation and used as such, however, optionally it can also, prior to its use, be dehydrated, preferably by using a pressure filtration, in particular by means of a chamber filter press or a membrane filter press as well as alternatively by using a vacuum belt filter or a centrifuge, optionally washed with water and thereafter carefully dried at a temperature of below 100°C, preferably between 30 and 60°C and crushed, preferably milled. After separation, dehydrating and drying the precipitate can also
  - 30

be processed at a temperature of from 100 to 500°C, preferably from 100 to 200°C, and crushed, preferably milled.

5 The precipitation reaction in step (c) is preferably carried out continuously in a processing zone, in particular in stirred containers while stirring or in several processing zones, in particular in several containers in sequence, while stirring.

10 The precipitation in step (c) is preferably carried out within a reaction time of from 5 to 3000 min, in particular from 120 to 600 min, at a temperature of preferably from 5 to 60°C, in particular from 20 to 40°C.

15 The precipitate produced according to the process of the present invention after the dehydration can also be suspended by using proper dispergators and it can be used in the form of a filler or spreading pigment suspension for producing pulp, paper, paperboard or card as well as for the production of paints and lacquers, construction materials, such as mortars.

20 A further subject-matter of the invention is the use of the crystal water-containing products produced as described above as a flame-retardant filler for fire-protecting construction materials, insulating materials, mortars, wallpapers, paperboards, papers, for the production of paints and lacquers, as a filler for the production of plasterboards and construction slabs, respectively, or as a hydraulically active additive for producing swelling cements, swelling plasters, screeds and mortars as well as for microfiber armation of cements and mortars.

25 It is to be noted that the precipitates on the basis of a crystalline crystal water-containing calcium compound obtainable according to the process of the present invention can be used both in the form of a slurry or suspension and in the form of a dry solid or also in calcined and milled form as a filler and addi-  
30 ve, respectively.

According to a further aspect the present invention relates to the use of the crystal water-containing calcium compounds prepared according to the present invention as a precipitate in a dehydrated and milled state as an additive in the construction materials industry, preferably as a swelling component for ce-  
 5 ments and for the explosion-protected blasting as well as for microfiber armati-  
 on of cements or mortars.

The invention is illustrated in detail in the following examples, however, without being limited thereto.

10

### Example 1

Into a stirred vessel one after another are added:

15

4000 kg of water,  
 1500 kg of an aluminum pickling lye containing 6 % by weight of Al and 18 %  
 by weight of  $\text{Na}_2\text{O}$   
 450 kg of calcium oxide in the form of chalk milk suspended in water

20

By a chemical reaction a white calcium aluminatehydrate pricipitate containing crystallisation water is formed. After a stirring time of 200 min the alkalinely dis-  
 solved aluminum in an amount of more than 90 % has been transformed into a  
 hardly soluble calcium aluminate-hydrate precipitate. The precipitate is separa-  
 ted as a filter cake, washed with water and processed as follows:

25

- a) either dried and optionally milled
- b) or suspended in water and further chemically treated according to step  
 (c) of the process.

30

The obtained compound was as follows:



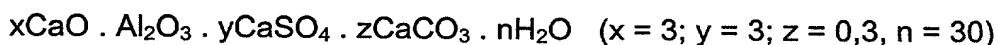
Example 2

Into a stirred vessel one after another are added:

- 5    8000 kg of water  
      1000 kg of suspended calcium aluminatehydrate precipitate containing  
      6 weight% of Al and 14 weight% of CaO, prepared according to  
      example 1  
      350 kg of sulfuric acid containing 45 weight% of SO<sub>4</sub>  
 10   250 kg eloxalic acid<sup>\*)</sup> containing 1 weight% of Al and 20 weight% of SO<sub>4</sub>

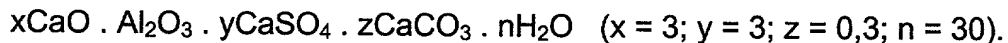
<sup>\*)</sup> ————— aluminum-containing sulfuric acid derived from an eloxation facility.

- By a chemical reaction an extra white crystallisation water-containing calcium  
 15   aluminatesalt precipitate is formed. After a stirring time of 300 min the dissolved  
      sulfate in an amount of more than 90 % has been transformed into a hardly  
      soluble calcium aluminatesalt precipitate. The precipitate is separated as a filter  
      cake and crushed or suspended or optionally dried and dry-milled.  
 20   The obtained compound was as follows:

Example 3

- 25   This example was carried out similar to example 2, however by using 300 kg of  
      plaster containing 50 weight% of SO<sub>4</sub> instead of 350 kg of sulfuric acid contain-  
      ing 45 weight% of SO<sub>4</sub>. The other process measures were identical to those in  
      example 2.

- 30   The obtained compound was as follows:





## Claims

1. A process for producing calcium compounds containing water of crystallisation, the process being characterized in that

a) by a chemical reaction between an aqueous alkaline solution of sodium aluminate and a solid or dissolved and suspended, respectively, calcium (hydr)oxide in the presence of carbon dioxide or carbonate a precipitate of a mixture of calcium aluminatohydrates having the following modular formula is formed:



b) the thus obtained precipitate, in a manner known per se, is separated by sedimentation, dehydrated, optionally washed with water and the thus obtained filter cake is either dried and/or calcined and/or milled,

c) or the filter cake obtained in step (b) in a wet and/or dried form is suspended in water and added with at least one mineral acid and/or at least one salt thereof for forming a calcium aluminatesalt precipitate containing water of crystallisation, the precipitate is separated by sedimentation, dehydrated, optionally washed with water and the thus obtained filter cake is crushed and optionally dried and/or milled.

2. The process according to claim 1, characterized in that as an aqueous alkaline sodium aluminate solution a waste pickling lye is used as obtained by surface-treatment of aluminum metal.

3. The process according to claim 1 or 2, characterized in that an aqueous alkaline sodium aluminate solution and a waste pickling lye, respectively, is

used wherein  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  are present in a mole ratio of (1.0 to 10.0):1, preferably of (1.2 to 2.5):1.

4. The process according to at least one of claims 1 to 3, characterized in  
5 that in step (a) an aqueous alkaline sodium aluminate solution is used as a starting material and calcium (hydr)oxide is added thereto.

5. The process according to at least one of claims 1 to 3, characterized in  
10 that in step (a) calcium (hydr)oxide is used as a starting material and then the aqueous alkaline sodium aluminate solution is added.

6. The process according to claim 4 or 5, characterized in that from 2 to 8  
15 mole of  $\text{CaO}$  equivalents, preferably from 3 to 5 mole of  $\text{CaO}$  equivalents, based on 1 mole of  $\text{Al}_2\text{O}_3$  equivalent, are added.

7. The process according to at least one of claims 1 to 6, characterized in  
20 that the precipitation of the precipitate in step (a) is carried out within a reaction time of from 5 to 3000 min, preferably from 60 to 600 min, at a temperature of from 5 to 60°C, preferably from 30 to 50°C.

8. The process according to at least one of claims 1 to 7, characterized in  
25 that the calcium aluminatehydrate precipitate in step (b) is mechanically dehydrated, preferably by using a pressure filtration, in particular by using a chamber filter press or a membrane filter press and, alternatively, by using a vacuum belt filter or a centrifuge.

9. The process according to claim 8, characterized in that the dehydrated  
30 calcium aluminatehydrate precipitate at a temperature of < 100°C is dried and crushed, preferably milled.

10. The process according to claim 8, characterized in that the dehydrated  
calcium aluminatehydrate precipitate at a temperature of from 100 to 1300°C,

preferably from 100 to 500°C, is dried and calcined, respectively, and crushed, preferably milled.

11. The process according to at least one of claims 1 to 8, characterized in that the dehydrated and optionally washed filter cake of step (b) is suspended in water and added with at least one mineral acid and/or at least one salt thereof to form an extra white calcium aluminatesalt precipitate containing water of crystallisation, the precipitate optionally being further processed according to claim 9 or 10.
12. The process according to claim 11, characterized in that as a mineral acid hydrochloric acid, hydrofluoric acid, sulfuric acid, silicic acid and/or carbonic acid and salts thereof, respectively, in particular their alkaline metal salts, alkaline earth metal salts and aluminum salts are used.
13. The process according to claim 12, characterized in that as a mineral acid a sulfuric acid containing aluminum, preferably a waste acid derived from eloxal plants is used.
14. The process according to claim 11, characterized in that in step (b) a sulfate is added to the filter cake suspended in water in a ratio of 1 part by weight of Al to 4 to 7 parts by weight of  $\text{SO}_4$ , based on the total aluminum content.
15. The process according to claim 14, characterized in that anions of the further mineral acid(s) mentioned in claim 12 and/or salts thereof are additionally added in amounts of 1 part by weight of Al to 0.5 to 10 parts by weight of anions, based on the total aluminum content of the suspension.
16. Use of the products obtained in the process according to any of claims 1 to 15 in the form of an aqueous suspension and/or in solid form as an extra white pigment for surface-coating of paper or as a filler in the production of pa-

per or in the production of paints and lacquers, preferably for indoor and outdoor uses.

17. Use of the products obtained in the process according to any of claims 1  
5 to 15 as a flame-retardant filler for fire-protecting construction materials, insulating materials, mortars, wallpapers, paperboards, papers, for the production of paints and lacquers, as a filler for producing plasterboards or building slabs or as an hydraulically active additive for producing swelling cements, swelling  
10 plasters and screeds, for microfiber armation of cements and mortars or as a swelling component for the production of explosion-protected explosives.
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## DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

(X) Original    ☐ Supplemental    ☐ Substitute    ☐ PCT    ☐ DESIGN

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: PROCESS FOR PRODUCING CALCIUM COMPOUNDS CONTAINING WATER OF CRYSTALLIZATION

of which is described and claimed in:

☐ the attached specification, or

☐ the specification in application Serial No. \_\_\_\_\_, filed \_\_\_\_\_, and with amendments through \_\_\_\_\_, or

☒ the specification in International Application No. PCT/EP98/07174, filed November 10, 1998, and as amended on (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Warren M. Chock, Jr., Reg. No. 33,367; Nils Pedersen, Reg. No. 33,145; Charles R. Watts, Reg. No. 33,142; and Michael S. Huppert, Reg. No. 40,268, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., as well as any other attorneys and agents associated with Customer No. 000513, to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys and agents named herein to accept and follow instructions from RUSCHKE, HARTMANN, BECKER as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

<b>Residence &amp; Citizenship</b>	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
<b>Post Office Address</b>	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


1st Inventor [Signature] Date 16.05.2001  
JOSEF LEHMKEUHL  
2nd Inventor [Signature] Date 09.05.2001  
ANGEL PENDEL  
3rd Inventor [Signature] Date 10.05.2001  
HUBERT PINGS  
4th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
5th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
6th Inventor \_\_\_\_\_ Date \_\_\_\_\_

The above application may be more particularly identified as follows:

U.S. Application Serial No. \_\_\_\_\_ Filing Date \_\_\_\_\_

Applicant Reference Number H 1243-PCT Any Docket No. \_\_\_\_\_

Title of Invention PROCESS FOR PRODUCING CALCIUM COMPOUNDS CONTAINING WATER OF CRYSTALLIZATION

Direct Correspondence to Customer No:  <b>000513</b> PATENT TRADEMARK OFFICE	Direct Telephone Calls to:  WENDEROTH, LIND & PONACK, L.L.P. 2013 K Street, N.W., Suite 800 Washington, D.C. 20006-1021  Phone: (202) 721-6200 Fax: (202) 721-6230
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Full Name of First Inventor	FAMILY NAME <b>LEHMKUHL</b>	FIRST GIVEN NAME <b>Josef</b>	SECOND GIVEN NAME
Residence & Citizenship	CITY <b>Hofheim</b>	STATE OR COUNTRY <b>Germany</b>	COUNTRY OF CITIZENSHIP <b>Germany</b>
Post Office Address	ADDRESS <b>Königsteinerstrasse 33, D-65719 Hofheim, Germany</b>	CITY	STATE OR COUNTRY ZIP CODE
Full Name of Second Inventor	FAMILY NAME <b>FENDEL</b>	FIRST GIVEN NAME <b>Ansgar</b>	SECOND GIVEN NAME
Residence & Citizenship	CITY <b>Dortmund</b>	STATE OR COUNTRY <b>Germany</b>	COUNTRY OF CITIZENSHIP <b>Germany</b>
Post Office Address	ADDRESS <b>Friedenstrasse 13, D-44139 Dortmund, Germany</b>	CITY	STATE OR COUNTRY ZIP CODE
Full Name of Third Inventor	FAMILY NAME <b>BINGS</b>	FIRST GIVEN NAME <b>Hubert</b>	SECOND GIVEN NAME
Residence & Citizenship	CITY <b>Lünen</b>	STATE OR COUNTRY <b>Germany</b>	COUNTRY OF CITIZENSHIP <b>Germany</b>
Post Office Address	ADDRESS <b>Brunnenstrasse 138, D-44536 Lünen, Germany</b>	CITY	STATE OR COUNTRY ZIP CODE
Full Name of Fourth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE
Full Name of Fifth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE
Full Name of Sixth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME